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Influence of Anchor Block Size on the Thickness of Adsorbed Block Copolymer Layers

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We present surface force data on three different polystyrene/poly(2-vinylpyridine) block copolymers (PS/P2VP) with a fixed size of the nonadsorbing PS block but widely varying sizes of the adsorbing P2VP block. With respect to the sizes of the two blocks, they range from moderately to highly asymmetric. The equilibrium force profiles are almost overlapping, which means that the variation in layer thickness is very small over a large range of anchor block size. This finding is in disagreement with the predictions of simple scaling models for polymer brushes. However it agrees with findings from neutron reflectivity data on a comparable series of PS/P2VP block copolymers. We also find agreement with recent neutron reflectivity experiments on poly(dimethylsiloxane)/polystyrene and with self-consistent field calculations on selectively adsorbed block copolymers.

Introduction

Adsorption of polymers at solid–liquid interfaces is essential for the steric stabilization of colloidal dispersions.¹ Homopolymers are often used for this purpose although—depending on the surface coverage—these may also give rise to destabilization by bridging (the simultaneous adsorption of one chain to two colloidal particles). Diblock copolymers with one adsorbing and one nonadsorbing block may be a better choice. The adsorbing block (“anchor block”) sticks to the surface, thereby fixing one end of the nonadsorbing block (“buoy block”) near the surface. If the anchor block is strongly adsorbing and assumed to form a thin collapsed layer on the surface, then the buoy block can be considered to be virtually end-grafted. Due to the nonadsorbance of the buoy block, bridging is avoided and a monotonous repulsion between layers will result under good solvent conditions. The range of this repulsion depends on the thickness of the adsorbed layer. We will consider the dependence of this layer thickness on the size of the anchor block, at fixed buoy block size.

For a layer of truly end-grafted polymer chains at high density (often called a polymer brush), the layer thickness is given by^{2,3}

$$L \cong N\sigma^{1/3} \quad (1)$$

where N is the degree of polymerization and σ the surface density (the number of chains per unit area). Such ideal brush behavior is often assumed for block copolymers with anchor blocks that are short relative to the buoy blocks.

Hadziioannou et al.⁴ performed the first experiments on PS/P2VP block copolymers adsorbed on mica from toluene. Toluene is a good solvent for PS and a nonsolvent for P2VP. They proposed a model in which the P2VP blocks are assumed to form adjacent collapsed disks on the surface, due to the high adsorption energy resulting

from the incompatibility of P2VP with toluene. The crowding of the collapsed P2VP blocks restricts the lateral space available for each PS block. The PS blocks then tend to stretch in order to diminish the unfavorable osmotic interactions resulting from lateral overlap. The entropy loss associated with the stretching must be outweighed by the adsorption energy of the P2VP blocks. In this model the surface density σ is solely determined by the size of the P2VP block. The characteristic size of the P2VP anchor block in toluene (a nonsolvent) is taken as the radius of gyration of a collapsed globule, given by

$$R_{G,P2VP} = N_{P2VP}^{1/3} a_{P2VP} \quad (2)$$

The area occupied by such a globule scales with the square of this quantity, hence

$$\sigma \cong \frac{1}{R_{G,P2VP}^2} \cong N_{P2VP}^{-2/3} \quad (3)$$

This leads to the following scaling relationship between the layer thickness and the number of segments in each of the blocks⁴

$$L_0 \cong N_{PS} N_{P2VP}^{-2/9} \quad (4)$$

The linear scaling of L_0 with N_{PS} was found to be in reasonable agreement with the experimental results.⁴ The scaling of L_0 with N_{P2VP} was not investigated however. More recent experiments^{5,6} have shown that the linear scaling of L_0 with N_{PS} breaks down if $N_{PS} \gg N_{P2VP}$. Our aim is to investigate if the scaling of L_0 with N_{P2VP} obeys eq 4. But first we will discuss some symmetry considerations

Two extremes of asymmetry can be distinguished as depicted schematically in Figure 1. If $N_{PS} \gg N_{P2VP}$ (Figure 1a) the P2VP disks are much smaller in the lateral direction than the PS buoy blocks. This means that at full surface coverage of the anchor disks, the buoy blocks would have to be highly stretched to fit into the small lateral space dictated by the disks. However the large loss of entropy caused by this stretching cannot be

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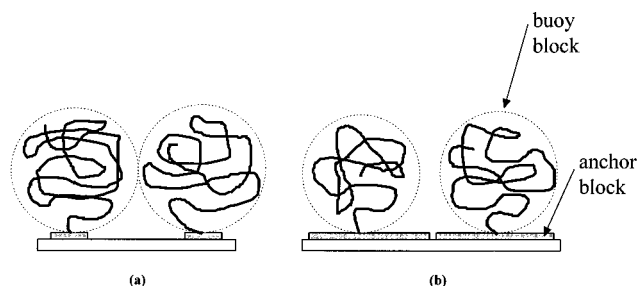


Figure 1. Two extremes of asymmetry of block copolymers and the resulting structures. The buoy-dominated (a) and anchor-dominated (b) regimes.

Table 1. Characteristics of the Block Copolymers Used in This Study

polymer	N_{PS}	N_{P2VP}	M_w/M_n
75/3.4	750	34	1.04
75/32	750	320	1.10
75/102	750	1020	1.12

compensated by the small adsorption energy of the anchor block. In this case the buoy blocks determine the surface density, which will be below full surface coverage. This is the *buoy-dominated regime*. If $N_{P2VP} \gg N_{PS}$ (Figure 1b) the lateral size of the P2VP disks is so large that the PS buoys are not forced to overlap. There is no driving force for stretching and the buoy blocks form separate "mushrooms" with a radius of the order of the radius of gyration. This is the *anchor-dominated regime*. In between these two extremes, at more or less comparable sizes of the two blocks, the surface density will be anchor-dominated as long as the adsorption energy is sufficient to compensate for the loss of entropy due to stretching of the buoy. Here we consider how the layer thickness changes with the size of the anchor block (N_{P2VP}) at fixed buoy block size (N_{PS}). To express the (a)symmetry of a selectively solvated block copolymer chain in a quantitative way, we use the "solvent-induced asymmetry" parameter β .^{7,8} This parameter is defined as the ratio of the projected areas of both blocks:

$$\beta = \frac{R_{G,PS}^2}{R_{G,P2VP}^2} = \frac{N_{PS}^{6/5}}{N_{P2VP}^{2/3}} \quad (5)$$

The segment sizes of PS and P2VP are assumed equal in this equation. To express the surface density of polymer chains, we use the reduced surface density defined as

$$\sigma^* = \sigma/\sigma_{ol} \quad (6)$$

where σ is the actual surface density and σ_{ol} the overlap density, the density above which the PS blocks are forced to overlap

$$\sigma_{ol} = \frac{1}{\pi R_{G,PS}^2} \cong N_{PS}^{-6/5} \quad (7)$$

The radius of gyration of the PS block can be determined from⁹

$$R_{G,PS} = 1.86 N_{PS}^{0.595} \text{ (\AA)} \quad (8)$$

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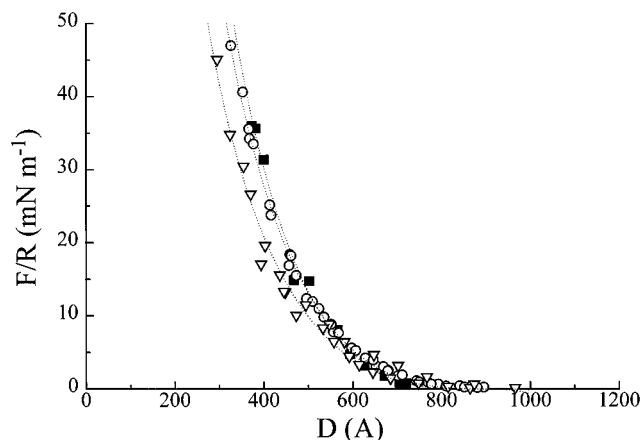


Figure 2. Force-distance profiles for the three block copolymers: \circ , 75/3.4; \blacksquare , 75/32; ∇ , 75/102. The solid lines are fits to the profiles obtained by using eq 9 as explained in the text.

Experimental Section

The characteristics of the block copolymers used in this study are shown in Table 1. The notation in column 1 will be used to refer to them. Grade 4 ASTM V-2 clear and slightly stained Muscovite ruby-red mica is used as the substrate surface for the experiments. The surface forces apparatus¹⁰ is equipped with a small (10 mL) liquid cell to reduce the volumes of liquid needed. The liquid cell and its internal parts are cleaned in 30% HNO₃ solution overnight and then thoroughly washed with distilled water and alcohol and finally blown dry with pressurised high-purity nitrogen. Surface forces are first recorded in pure toluene to check for the cleanliness of the solvent and the absence of any surface contamination. Polymer solution is then added to the liquid cell to a final concentration of 0.05 mg/mL. Surface forces are first recorded after 2 h and then at intervals of 24 h over a period of 4 days in total. Compression/decompression cycles are recorded to check for the existence of hysteresis.

Results and Discussion

The force profiles for the three block copolymers, recorded after the longest equilibration time (4 days), are shown in Figure 2. As can be seen the profiles are almost overlapping, and the layer thickness values derived from them are all close to 450 Å. No hysteresis between compression and decompression is observed, except when the layers are compressed very strongly (up to 10^{-1} N m⁻¹). After 24 h the layers have apparently reached their equilibrium thickness, except for the 75/102 layer, which continues to grow slightly over a period of 3 days. The time evolution of the layer thickness of the 75/102 is shown by the force profiles in Figure 3. It is clear that sufficient time should be allowed for the adsorption process in order to reach the equilibrium layer thickness. From the time evolution of the 75/102 it appears that an incubation time of 4 days is sufficient to reach equilibrium.

A comparison between theoretical expectations and experimental findings is presented in Table 2. Since direct measurements of the surface densities of our block copolymers are not available, we have used values calculated from the fitting equation given by Webber et al.¹¹ This fitting equation is based on the data of Parsonage et al.⁸ for PS/P2VP block copolymers over a wide range of β . Since our block copolymers are all inside this range, we trust that these fitted surface densities, σ_{fit} , are close to the actual values. The tabulated values σ^* are calculated from the σ_{fit} values.

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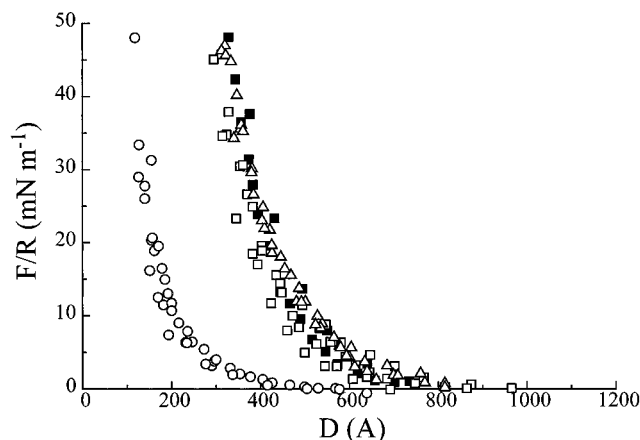


Figure 3. Force profiles for the 75/102 after several incubation times: ○, after 2 h; □, after 1 day; △, after 3 days; ■, after 4 days.

Table 2. Comparison between Theoretical and Experimental Data for the Series of PS/P2VP Block Copolymers with Fixed $N_{PS} = 750$ and Varying P2VP Block Lengths

polymer	β	σ^* ($\text{m}^{-2} \times 10^{-16}$)	L_0 (Å)	L_{sc}^I (Å)	L_{sc}^{II} (Å)
75/3.4	269	4.7	455	713	499
75/32	60	3.1	433	433	433
75/102	27	1.8	458	335	364

The experimental layer thickness values L_0 were determined from the force profiles of Figure 2 by fitting them with eq 9 (see ref 12), which is, strictly, derived for an ideal brush, but can be expected to be valid as long as $\sigma > \sigma_{ol}$

$$\frac{F}{RkT} = \frac{CNL_0^2\sigma}{L_c^2} \left(\frac{5}{9} \left(\frac{L_0}{D} + \left(\frac{D}{L_0} \right)^2 - \frac{1}{5} \left(\frac{D}{L_0} \right)^5 \right) - 1 \right) \quad (9)$$

where F is the normal force, kT the thermal energy, R the (mean) radius of curvature of the surfaces, C a polymer-specific constant, N the degree of polymerization, L_0 the layer thickness, L_c the contour length of the buoy block ($L_c = Na$), and D the distance between the supporting surfaces. L_0 can be determined as a separate parameter in the fitting procedure.

Table 2 compares the experimental layer thickness values L_0 to theoretical layer thickness values L_{sc}^I and L_{sc}^{II} . The L_{sc}^I values reflect the situation where the surface density is solely determined by the anchor blocks assuming that they fill the surface completely (eq 4). The L_{sc}^{II} values reflect the situation of a generalized brush, by using the actual surface density (σ_{fit}) without making assumptions about the structure of the anchor blocks (eq 1).

Since eqs 4 and 1 are scaling relations, the scaling coefficients can be used as adjustable parameters. The scaling coefficients of eqs 4 and 1 were chosen such that $L_{sc}^I(75/32) = L_{sc}^{II}(75/32) = L_0(75/32)$.

As can be seen from Table 2, the value of σ^* exceeds unity for all three block copolymers. Thus some amount of stretching is anticipated even for the block copolymer with the largest anchor block. From the values of L_{sc}^I it is clear that the model of close-packed anchor blocks—filling the surface completely—is inconsistent with the experimental findings. According to this model, the layer thickness should vary by almost 400 Å over the range of β values covered in this study. It is clear that this is far more than the variation in the experimental layer thickness, even for a worst case error of 10% in L_0 . From the

Table 3. Comparison between Theoretical and Experimental Data for the Series of PS/P2VP Block Copolymers with Fixed $N_{PS} = 600$ and Varying P2VP Block Lengths (from ref 13)

polymer	β	σ_{fit}^* ($\text{m}^{-2} \times 10^{-16}$)	σ_{refl}^* ($\text{m}^{-2} \times 10^{-16}$)	L_0 (Å)	L_{sc}^I (Å)	L_{sc}^{II} (Å)
60/5	159	4.3	5.2	320	625	472
60/30	48	2.7	3.4	440	420	401
60/60	30	1.9	1.5	360	360	360
60/120	19	1.3	1.0	360	309	317

values of L_{sc}^{II} it can be seen that releasing the constraint of full surface coverage decreases the range of the thickness variation. However the agreement is still unsatisfactory. The discrepancies between L_0 , L_{sc}^I , and L_{sc}^{II} are largest for the block copolymer with the smallest anchor block.

Our findings are in good agreement with the neutron reflectivity results of Field et al.,¹³ who studied the same system over a comparable range of asymmetries and block sizes. The block copolymers used in their experiments have a fixed PS block of $N_{PS} = 600$ and P2VP blocks of $N_{P2VP} = 50, 300, 600$, and 1200. They found that the block copolymer with the smallest P2VP block was best fitted with a density profile for a brush, whereas the other three, with the larger P2VP blocks, were best fitted with a mushroom-type profile. The layer thicknesses, as determined from the reflectivity profiles, are relatively constant over the range studied. Their results are summarized in Table 3 in a similar fashion as in Table 2. The reduced surface densities based on the experimental surface density values from the neutron reflectivity data are also shown. Although σ_{fit}^* and σ_{refl}^* follow the same trend with increasing β , their absolute values differ considerably. Since the σ_{fit}^* values are believed to be more accurate, they have been used in the calculation of L_{sc}^{II} . The values of the scaling coefficients for L_{sc}^I and L_{sc}^{II} were taken such that $L_{sc}^I(60/60) = L_{sc}^{II}(60/60) = L_0(60/60)$. Table 3 shows that the L_{sc}^I and L_{sc}^{II} values are much larger than L_0 values for the block copolymer with the smallest anchor block. The correspondence of the 60/30 and 60/120 is somewhat better.

All of the block copolymers in Table 3 have reduced surface densities exceeding unity. Even so, the 60/30, 60/60, and 60/120 were found to be best fitted with mushroom-type profiles. The 60/5 was found to be better fitted with a brush-type profile, but it is not stretched more than the others. The main conclusion drawn by Field et al. is that the structure formed by a PS/P2VP block copolymer is not that of an idealized highly stretched brush but instead the adsorbed layers are in a crossover region between mushrooms and brushes. Our results provide additional evidence for this conclusion. In a recent article, Webber et al.,¹¹ using hydrodynamic thickness measurements investigated the dependence of L_0 on N_{P2VP} for highly asymmetric PS/P2VP block copolymers with buoy blocks of $N_{PS} \approx 430$ and short anchor blocks of $N_{P2VP} = 9, 50, 57$, and 73. Over this small range of anchor block length, they find a rather sharp maximum in the layer thickness around $N_{P2VP} = 50$. Consequently, it could be that the 75/3.4 and the 60/5 are just outside the region of maximal layer thickness. Nevertheless it is clear that ideal brush behavior is not a general feature of PS/P2VP block copolymers with short anchor blocks.

Kent et al.^{14,15} have performed neutron reflectivity experiments, on a PDMS/PS block copolymer at the

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interface of ethylbenzoate (EB) and air in a Langmuir–Blodgett trough. EB is a good solvent for PS and a bad solvent for PDMS. The PDMS block adsorbs at the EB–air interface and anchors the PS buoy block. The advantage of using a Langmuir–Blodgett trough is that the surface density can be changed at fixed anchor block size, by moving the barrier of the trough to compress or decompress the layer. The neutron reflectivity data were obtained over a wide range of surface densities. In terms of the reduced surface density, σ^* , the range was approximately from 1 to 12. Over this decade of surface density, the variation in the layer thickness was found to be only 30%. Moreover no stretching was apparent over the range $1 < \sigma^* < 2$, i.e., at moderate overlap between neighbouring buoy blocks. Equation 1 was not obeyed over the range $1 < \sigma^* < 12$. The following empirical scaling relationship was found instead:

$$L_0 \cong N_{\text{PS}}^{0.86} \sigma^{0.22} \quad (10)$$

Equation 10 predicts a much weaker dependence of L_0 on N_{PS} and σ than eq 1. By examination of the data from a number of different studies, it was shown that for block copolymers adsorbed from a dilute solution in a good solvent, the maximum value of σ^* is around 15. Self-consistent field calculations on selectively adsorbed block copolymers by Baranowski et al.¹⁶ corroborate eq 10. The conclusion of Kent et al. is that there are three regimes of stretching. Roughly speaking $\sigma^* < 2$ corresponds to the *mushroom regime* (no stretching), $2 < \sigma^* < 20$ to the *intermediate (crossover) regime* (weak stretching), and σ^*

> 20 to the “*true*” *brush regime*, where the chains are highly stretched and approach the asymptotic brush limit of eq 1. The main conclusion to be drawn from this discussion is that block copolymers with short anchor blocks do not form true brushes by adsorption from a dilute solution.

Conclusions

The dependence of the layer thickness of adsorbed block copolymer layers of PS/P2VP on the size of the anchor block is more complicated than that predicted by models based on the packing of the P2VP blocks on the surface. Even if the constraint of full surface coverage is released, brushlike scaling of the layer thickness with respect to the surface density is not found. This corroborates earlier results obtained with neutron reflectivity, showing that even above the overlap density the layer structure can be fitted with mushroom-type profiles, except for surface densities far above the overlap density. Decreasing the size of the anchor block increases the surface density and makes the layer more brushlike as evidenced by the success of fitting with brush-type profiles. However the asymptotic brush limit seems to be out of reach for block copolymers adsorbed from dilute solution.

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